
III.A.1 Evaluation of a Functional Interconnect System for SOFCs

Objectives

Evaluate complex interconnect structures based on metallic substrates, including, but not limited to, clad and coated systems and SOFC sub-cell structures.

- Demonstrate the production of complex interconnect structures and systems.
- Evaluate the interactions of simple and complex interconnect systems with simulated local SOFC environmental conditions, including atmospheres and materials of construction expected to be in contact with interconnects.
- Quantify performance of simple and complex interconnect systems, particularly in the areas of electrical properties (ALC/Pitt) and layer adhesion (CMU/WVU).

Accomplishments

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- Successfully produced multi-layered clad interconnect structures and tested in simulated anode gas and dual atmosphere exposures, with initial results showing promise.

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- Applied novel processing to common ferritic stainless steels, resulting in the production of desired structures.
- Melted and processed novel stainless steel compositions.
- Exposed E-BRITE alloy (Fe-26Cr-1Mo) and model alloy RV 2103 (Fe-22Cr) specimens in simulated cathode gas environments for indentation spallation studies at Carnegie Mellon University. The exposures were designed to simulate actual exposures of up to 40,000 hrs at 800°C.
- Provided Type 430 substrates to Arcomac Surface Engineering for application of their coating systems.

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- Performed macro-scale indentation spallation tests on E-BRITE alloy (Fe-26Cr-1Mo) and model alloy RV 2103 (Fe-22Cr) specimens exposed by Allegheny Technologies, Inc. (ATI) in simulated cathode gas. Tracked spallation densities as a function of exposure time.
- Initiated macro-scale indentation tests on coated Type 430 specimens from Arcomac Surface Engineering (with substrates from ATI).
- Performed proof-of-concept nanoindentation tests on exposed E-BRITE alloy specimens from ATI. Identified cracking geometries needed for nanoindent modeling work.
- Initiated nanoindentation modeling to relate crack size measurements from tests to stress intensity factors and energy release rates.

West Virginia University

- Identified and tested several silver cermets as contact paste materials for SOFCs.
- Completed the study of evaporation characteristics and microstructure changes of sterling silver and pure silver under high-temperature exposure conditions.

Introduction

The interconnect is a critical part of planar solid oxide fuel cells (SOFCs). The interconnect serves to separate the fuel and oxidant gas streams and also collects the electrical output of the SOFC. A shift from relatively inert ceramic interconnects to metallic structures has been driven primarily by cost considerations. Interconnect alloy selection has been identified as one of two primary issues impeding the

commercialization of SOFCs [1]. High-temperature degradation due to surface oxidation is the primary form of attack. Oxides in general have poor electrical conductivity, leading to increased contact resistance as they form and get thicker. This degrades the output of the fuel cell over time and should be minimized.

In addition, oxides can spall due to high compressive residual stresses at room temperature, increases in oxide thickness, and/or changes in scale adhesion to the substrate. Chromia scales, which have higher conductivities than other oxides, can also experience evaporation at high temperature, with evaporated chromium degrading cathode performance. Successful low-temperature SOFC interconnect systems will have to address these concerns while minimizing cost.

Approach

The approach in this project is to address the evaluation of new ferritic stainless steel-based SOFC interconnect systems in an integrated way, using expertise from each of our four project participants. Allegheny Ludlum is studying new interconnect alloys and surface treatments to achieve optimal combinations of reduced chromia scale growth, spallation resistance and reduced chromia scale evaporation, while minimizing cost. This includes the development of novel clad systems and interactions with DOE laboratories and industrial collaborators developing interconnect coating systems. The University of Pittsburgh is performing dual atmosphere tests on clad systems from ALC and providing support for microstructural studies. Carnegie Mellon is testing interconnects for chromia scale spallation resistance using macro-scale and nano-scale indentation tests. The goal of these tests is to accelerate the evaluation of new interconnect systems and to understand mechanisms leading to premature interconnect failure by spallation. Tests include bare alloys from ALC and coated systems from DOE laboratories and industrial partners, using ATI alloy substrates. West Virginia University is studying silver cermet pastes to enhance the contact between interconnects and cathode materials. Fundamental studies of the performance of different paste compositions will be followed up by studies of paste/alloy combinations using alloys from ALC.

Results

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Clad panels were produced using a variety of alloys which are expected to be inert in the anode environment, notably nickel 201 (UNS N02201), oxygen-free copper (UNS C10100), and a commercially produced Ni-32Cu alloy (UNS N04400). Some panels

were also clad on the cathode side with oxidation-resistant nickel-base superalloys. Examples of two as-processed clad panels are shown in Figure 1. A test plan was formulated to determine the resistance to oxidation in simulated anode gas (SAG) and dual atmospheres, along with the effects of thermal cycling.

- Testing in SAG resulted in a significant reduction in weight gain as compared to a Type 430 stainless steel control sample, attributable to the cladding side exhibiting little to no oxidation. This can be seen visibly in Figure 2 for a nickel-clad stainless steel sample. Some accelerations in the rate of weight gain were noted, which is due to mixed oxide nodule formation on exposed Type 430 surfaces.
- Initial dual atmosphere results indicated that T430 stainless steel clad with copper or nickel resulted in no oxidation on the anode side. There was evidence of hydrogen migration to the air side, resulting in the formation of mixed oxide nodules and oxide blade-type features (Figure 3). The samples clad with the Ni-32Cu alloy formed a thin, adherent manganese oxide layer on the SAG side. Evidence of hydrogen migration on the air side is much reduced to a few scattered blade-like oxide grains (Figure 4). It is hypothesized that the MnO scale is helping to block transport of hydrogen across the interconnect.
- The thermal cycling tests indicated that differential thermal expansion between the clad outer layers

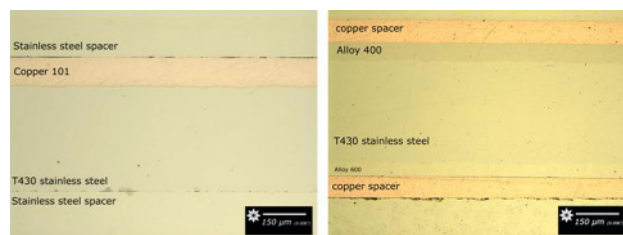


FIGURE 1. As-processed Clad Panels (light optical micrographs of polished metallurgical cross-sections): Bi-Layer Type 430 Stainless Steel Clad with Copper 101 Alloy on the Anode Side (left), Tri-Layer Type 430 Stainless Steel Clad with Ni-32Cu Alloy on the Anode Side and Ni-Base Superalloy 600 on the Cathode Side (right)



FIGURE 2. Example of a Clad Sample Exposed for 1,371 Hours at 800°C in SAG (Ar-4%H₂-3%H₂O): Type 430 Stainless Steel Substrate (left) and Nickel Cladding (right)

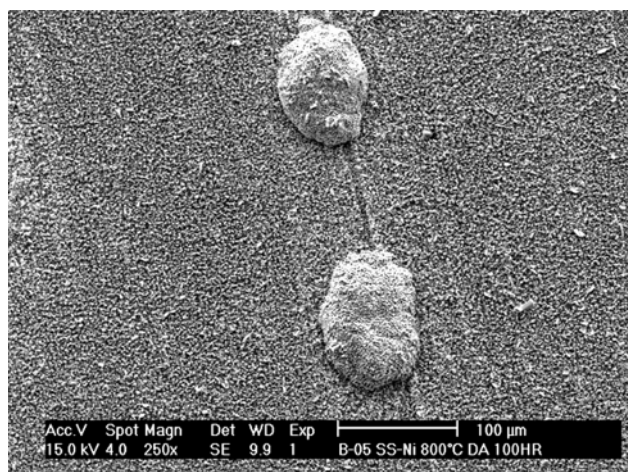


FIGURE 3. Oxide Scale as Formed on the Air Side of a Type 430 Stainless Steel Sample Clad with Nickel during a 100 Hour Dual Atmosphere Exposure at 800°C (surface SEM micrographs; stainless steel side exposed to air, nickel-clad side exposed to Ar-4% H_2 -10%H $_2$ O)

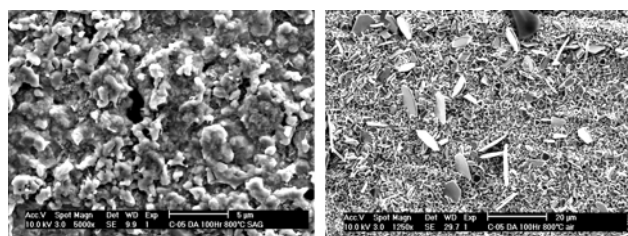


FIGURE 4. Oxide Scale as Formed on a Type 430 Stainless Steel Sample Clad with Ni-32Cu Alloy during a 100 Hour Dual Atmosphere Exposure at 800°C (surface SEM micrographs): Ni-32Cu Cladding (left, as exposed to Ar-4% H_2 -10%H $_2$ O), Type 430 Stainless Steel (right, as exposed to air)

and the inner core is not negligible. Some of the samples, notably the two-layer ones clad with Ni-32Cu, exhibited some curling.

Post-process treatments are being investigated in an attempt to improve the performance of typical ferritic stainless steels in the SOFC environment by mitigating the formation of electrically resistive oxides of aluminum and silicon at the scale/alloy interface.

- Samples of AL453 alloy, a Fe-22Cr-0.5Al alloy, were treated in an attempt to sequester aluminum in the form of stable particles. The initial results were successful. Measurements and calculations indicate that nominally all of the aluminum initially present in the substrate has been sequestered with a beneficial effect on ASR (Figure 5).
- Samples of Type 430 stainless steel (Fe-16.5Cr-0.3Si) were treated in an attempt to remove silicon from the surface without removing other elements,

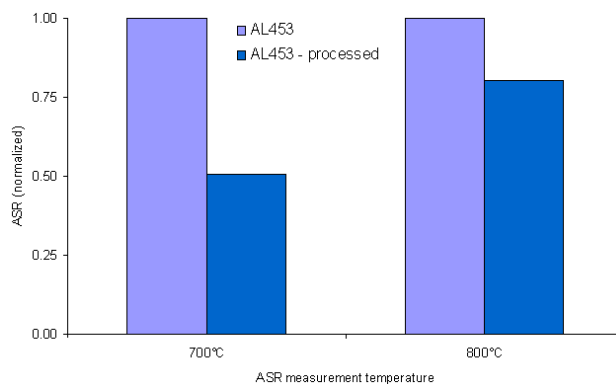


FIGURE 5. Effect of Surface Treatment on Relative ASR of AL453 Alloy

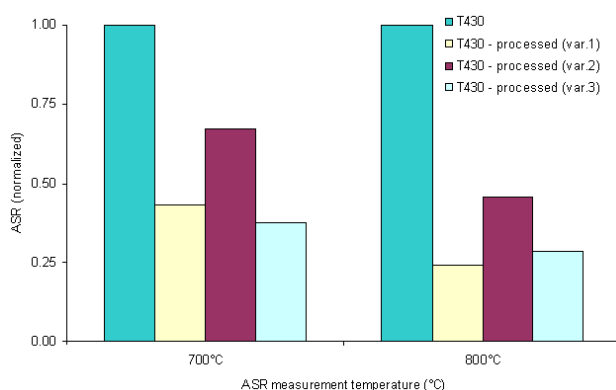


FIGURE 6. Effect of Surface Treatment (Three Variants) on Relative ASR of T450 Stainless Steel

notably chromium. The intent is to leave behind silicon-depleted metal. The initial results were successful, with scanning Auger microprobe analysis (SAM) indicating that silicon was depleted at the surface by a nominal factor of 40. Calculations indicate that the treatment as-applied is capable of removing approximately 40% of the total silicon in a 0.5 mm thick substrate. The effect is likely to be magnified near the surface due to the presence of a silicon depletion gradient. The effect on ASR was beneficial (Figure 6).

Base alloy development is progressing at ALC. Several heats have been melted, cast, and processed to flat rolled plates. Some surface issues were encountered and were bypassed by machining the plates after rolling. Testing is ongoing, with results expected by the end of September 2006 for monolithic samples and samples coated with oxidation-resistant layers and/or cathode contact paste. Two primary alloy compositions are being investigated:

- A superferritic stainless steel based on a modified E-BRITE composition. The goal is to produce

an alloy with the beneficial qualities of E-BRITE alloy, while improving the resistance to oxide scale evaporation and sigma formation.

- A Fe-Cr-Al alloy family containing a high level of rare earth metals.

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ATI is providing CMU with interconnect alloy specimens that have undergone exposures simulating 800°C for times up to 40,000 hours. Most exposures are being performed in lab air at 900°C. Specimens tested thus far are E-BRITE, having composition Fe-26Cr-1Mo-0.2Si, and RV 2103, a 21.8Cr-0.033Mn alloy with Ti, C, N, Ce, La, Al and Si in percentages of 0.02 or less. Specimens of RV 2103 were provided to yield a comparison between 26Cr and 22Cr alloys. Specimens were in the as-rolled condition, with ground finish rolls used for the final rolling operation. This yields a surface Ra of approximately 8 μm .

A macro-scale indentation test has been developed by the principle investigator J. Beuth and his students (under DOE and National Science Foundation support) for measuring the fracture toughness of interfaces between oxide scales and metallic substrates [2-4]. The test consists of indenting a coated or uncoated oxide/alloy system with a Bräle type conical indenter. The indenter penetrates the brittle coatings (if present) and oxide layer and plastically deforms the metallic substrate below. This plastic deformation induces compressive radial strains in the substrate. Because these strains are transferred to the oxide, they can act to drive its debonding. As illustrated in Figure 7 (as viewed from above), indentation induces a radial distribution of flaking-type spalls of the chromia scale. Systems with poor adhesion between the chromia and interconnect alloy exhibit a higher density of debonds and a larger radial extent of debonding. Image analysis allows the percentage of indentation-induced debonding to be quantified as a function of radial distance from the indent.

Each of the specimens sent to CMU has been subjected to macro-scale indentation testing. Results of debond density vs. radial distance from the indent center are still being analyzed. However, some initial observations and trends in the results are worth noting. First, E-BRITE specimens with short exposure times showed no debonding at all. In contrast, RV 2103 specimens subjected to the same exposures showed clear debonding, with the density of debonding increasing with exposure. It is clear that the E-BRITE alloy is much more resistant to spallation at early exposure times than the RV2103 alloy. Indentation tests on E-BRITE specimens exposed for extended exposure times have shown progressive increases in debond density with exposure time. Further analysis of these tests is underway.

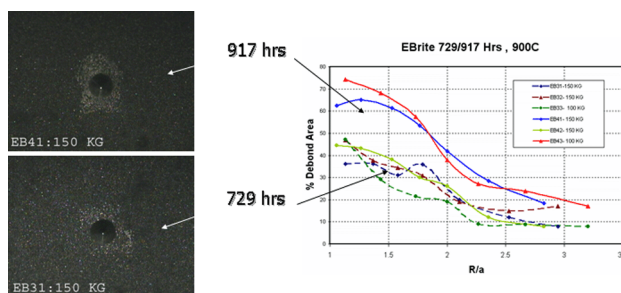


FIGURE 7. Indentation of E-BRITE specimens, as viewed from above. White areas indicate spalls induced by indentation strains. Image analysis yields a plot of debond percentage vs. normalized radius.

Macro-scale indent tests have also been performed on coated specimens from Arcomac Surface Engineering. These tests in the as-processed state will be followed up by exposures at ATI and indentation tests at CMU. A nano-scale indentation test is under development for use in combination with the macro-scale test, to probe toughnesses of chromia scales and chromia/alloy interfaces on a local scale. The test involves nanoindentation of the scale region of cross-sectioned samples. Nanoindents induce cracks in the scale or at the interface, and the length of the cracks can be related to the scale or interface toughness. This test is a means of measuring toughness directly, independent of scale residual stress and thickness which have a strong influence on toughness measurements on the macro scale.

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The experimental procedure for this research involved creating an environment similar to what the material would be exposed to in a real functioning fuel cell. This was accomplished using a simple tube furnace setup, illustrated in Figure 8. The tube furnace was maintained at 800°C, and air flow rate was controlled at approximately 3 l/min. The samples for this experiment were small sterling silver and pure silver plates. The main property of concern is the thickness reduction of the sample during exposure. Each week the samples were weighed, and the mass of the samples was taken as the average of several measurements. Samples were also evaluated using scanning electron microscopy (SEM) to evaluate microstructure changes taking place on the surface of the samples.

The evaporation characteristic of the sterling silver samples during high-temperature exposure was a relatively constant loss of mass over a duration of 27 weeks. Both types of pure silver samples (50 and 700 micron thickness) exhibited similar evaporation characteristics, with the rate of evaporation decreasing over time until a relatively constant rate was reached. A plot of the rates for the exposed samples is shown in Figure 9.

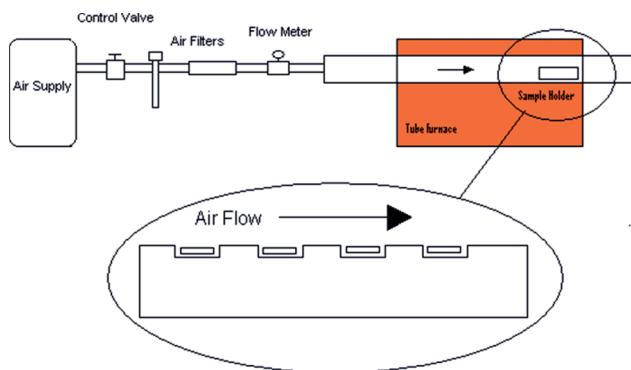


FIGURE 8. Experimental Setup for Exposure of Samples

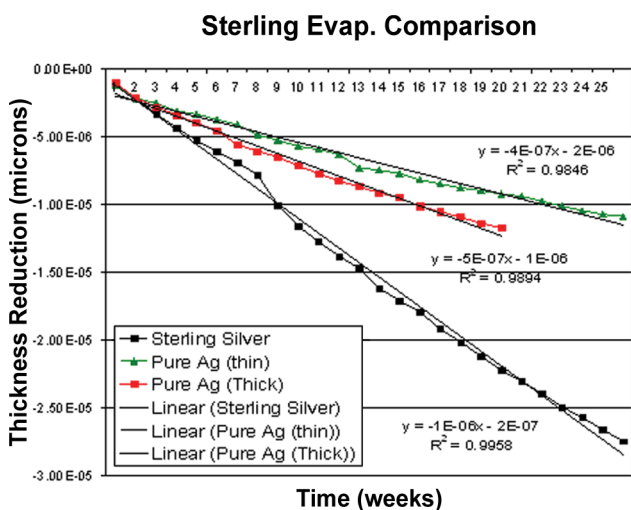


FIGURE 9. Comparison of Evaporation Rate for Various Samples

It can be seen in Figure 9 that the sterling sample evaporates the fastest, roughly 1 micron per week, while the pure samples evaporate much slower, roughly 0.4–0.5 microns per week. SEM analysis of the samples showed dramatic differences in the faceting behavior of the silver in the samples. Figure 10 illustrates the differing surface microstructures of the pure silver and sterling silver samples.

The faceting of the silver in the pure silver samples is much more dramatic than that of the sterling silver samples. It appears that through high-temperature exposure, the surfaces of the samples change until the surface eventually reaches an orientation that is not favorable to evaporation. It appears that the copper oxide in the sterling silver samples may inhibit the surface silver's ability to reach the desired orientation, whereas this is not the case in pure silver samples. Therefore, the sterling silver samples continue to lose

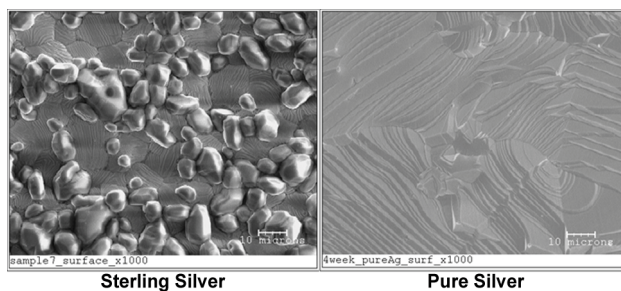


FIGURE 10. Comparison of Faceting of Sterling Silver and Pure Silver after High-Temperature Exposure

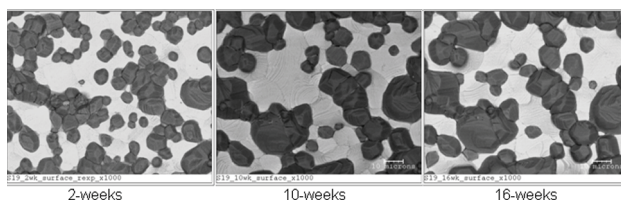


FIGURE 11. Time-Series SEM Backscatter Images of a Sterling Silver Sample

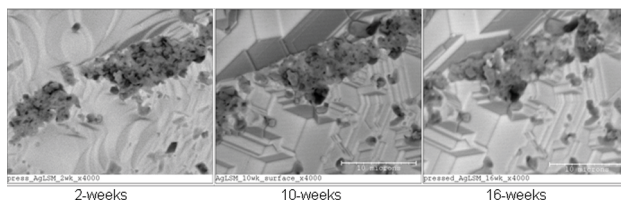


FIGURE 12. Time-Series SEM Backscatter Images of a Ag/LSM Sample

mass at a higher rate, while the pure silver sample's rate of evaporation is able to further decrease.

The evaporation test results and the follow-up SEM analyses indicated that copper oxide may be volatile when used as a protective oxide due to migration and agglomeration of the oxide particles. Figure 11 illustrates the behavior of the copper-oxide particles during long-term high-temperature exposure. Experiments were also carried out utilizing silver cermet with lanthanum strontium manganese oxide (LSM) to examine the volatility of LSM during high-temperature exposure. Figure 12 shows the SEM results for the samples. The LSM appears much more stable over long-term high-temperature exposure than copper oxide. For this reason as well as the evaporation characteristics of sterling silver, the focus of our future research will be on samples fabricated utilizing silver/LSM or silver/CeO.

Conclusions and Future Directions

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- Cladding appears to be a viable means of mitigating anode-side oxidation. Certain alloys may also be beneficial in reducing hydrogen migration.
- Novel post-processing appears to be capable of removing aluminum and silicon from finished stainless steel.
- Future laboratory evaluation will focus on electrical characterization of clad and post-processed materials, novel compositions, and complex sub-cell systems.

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- Macro-scale indent results are sensitive enough to show a clear difference in spallation behavior between 22Cr and 26Cr alloys at very short exposure times. This suggests that the test could be used for quick screening of new alloy systems for spallation resistance.
- Macro-scale indent tests performed on E-BRITE have shown a progressive increase in spallation density with exposure. The tests appear to be able to track progressive loss of debond resistance with exposure, for exposure times that would not yield any spontaneous spallation in standard thermogravimetric analysis tests.
- Macro-scale tests also appear well-suited for tracking debond resistance in coated specimens.
- Nano-scale indent tests have shown the ability to induce cracks in grown chromia scales, allowing the direct quantification of scale or interface toughness. These tests are under development.
- Fracture analyses of macro-scale tests will be performed to link test results to fracture toughnesses, for predicting times to spallation in alloy specimens.
- Coated specimens will be exposed and tested using the macro-scale test.
- Nano-scale testing will proceed on specimens subjected to a wide range of exposures to determine directly if scale or interface toughness is changing with exposure.

West Virginia University

- Surface orientation of silver appears to play an important role in the evaporation rate of any potential silver cermet materials.
- Due to migration and agglomeration of copper oxide particles at high temperature, silver cermet containing copper oxide particles is volatile when used as a contact paste material in a SOFC environment.

FY 2006 Publications/Presentations

1. Quarterly Report for 3rd calendar quarter 2005, including content from subcontractors CMU and WVU, 12/19/05.
2. Quarterly Report for 4th calendar quarter 2005, including content from subcontractors CMU and WVU, 01/25/06.
3. Project Fact Sheet, including content from subcontractors CMU and WVU, 02/22/06.
4. Quarterly Report for 1st calendar quarter 2006, including content from subcontractors CMU and WVU, 04/26/06.
5. "Evaluation of a Functional Interconnect System for SOFC's", Status Presentation at NETL Morgantown to Program Management. Meeting included presentations on the project from subcontractors CMU and WVU. 06/02/06.
6. J. L. Beuth, and N. Dhanaraj, Carnegie Mellon University, J. E. Hammer, S. J. Laney, F. S. Pettit, and G. H. Meier, University of Pittsburgh, "Interfacial Fracture Testing to Evaluate the Durability of SOFC Interconnect Alloys", ASM International/TMS, "Materials Solutions", Pittsburgh, PA, September 2005.
7. N. Dhanaraj, J. L. Beuth, G. H. Meier, F. S. Pettit, J. Hammer, and S. J. Laney, "Interfacial Fracture Testing to Evaluate the Durability of SOFC Interconnect Alloys", *Materials for the Hydrogen Economy* (J. J. Petrovic, I. E. Anderson, T. M. Adams, G. Sandrock, C. F. Legzdins, J. W. Stevenson, and Z. G. Yang, eds.), Proc. Materials Science and Technology 2005, Pittsburgh, PA, September 2005, pp 165-175.
8. "Elevated Temperature Environmental Degradation of Complex Interconnect Systems for Solid Oxide Fuel Cells", accepted for publication in the Fuel Cells and Energy Storage Systems Symposium at the MS&T 2006 Conference, Cincinnati, OH, October 15-19, 2006.

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3. Handoko, R.A., Beuth, J.L., Meier, G.H., Pettit, F.S. and Stiger, M.J., "Mechanisms for Interfacial Toughness Loss in Thermal Barrier Coating Systems," *Durable Surfaces* (D.R. Mumm, M.E. Walter, O. Popoola and W.O. Soboyejo, eds.), Proceedings of the Materials Division Symposium on Durable Surfaces, 2000 ASME International Mechanical Engineering Congress and Exposition, Orlando, November 2000, Trans Tech Publications, Switzerland, 2001, p. 165.
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